

# DEMONSTRATION OF PACKAGING OF FERNALD SILO I WASTE IN CHEMICALLY BONDED PHOSPHATE CERAMIC\*

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## ABSTRACT

This paper summarizes our experience in bench-scale packaging of Fernald Silo I waste in chemically bonded phosphate ceramics. The waste was received from the Fernald Environmental Management Project (FEMP), and its treatability was studied in our laboratory. This waste contained  $\text{As}^{5+}$ , Ba,  $\text{Cr}^{6+}$ , Ni, Pb,  $\text{Se}^{4+}$ , and Zn as the hazardous contaminants. In addition, the total specific activity of all the radioactive isotopes in the waste was  $3.85 \mu\text{Ci/g}$ , of which that of radium alone was  $0.477 \mu\text{Ci/g}$ . This indicated that radon (a daughter product of the radium) in the waste could present a serious handling problem during this study. For this reason, the waste was handled and stored in a flowing-air glovebox. We made waste form samples with an actual waste loading of 66.05 wt.% and subjected them to the Environmental Protection Agency (EPA) Toxicity Characteristic Leaching Procedure (TCLP). The results showed excellent stabilization of all contaminants. Actual levels detected in the leachate were well below the EPA's most stringent Universal Treatment Standards and in almost all cases were one order of magnitude below this limit. Radioactivity in the leachate was also very low. Alpha activity was  $25 \pm 2.5 \text{ pCi/mL}$ , while beta activity was  $9.81 \pm 0.98 \text{ pCi/mL}$ . This very low activity was attributed to the efficient stabilization of radium as insoluble radium phosphate in the waste form, thus prohibiting its leaching. This study indicates that the chemically bonded phosphate ceramic process may be a very suitable way to package Silo I waste for transportation and storage or disposal.

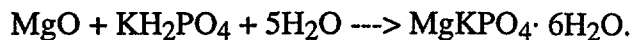
## INTRODUCTION

Fernald Silo wastes are residues from the processing of pitchblende ores during 1949-1958. The wastes are stored in silos in Operable Unit 4 (OU4) at DOE's Fernald Experimental Management Facility (FEMP) in Ohio.

Recently, the Mixed Waste Focus Area (MWFA) of DOE funded a feasibility project to assess several technologies to treat the wastes from these silos. The chemically bonded phosphate

ceramic (CBPC) process developed at Argonne National Laboratory [1-3] was one such technology. This paper provides an overview of this work on Silo I waste.

The CBPC process is based on acid-base reactions used to form compounds that mimic phosphate minerals found in nature and that have very low solubility. It is based on the reaction between calcined magnesium oxide (MgO) and a solution of monopotassium phosphate ( $\text{KH}_2\text{PO}_4$ ). The reaction product is magnesium potassium phosphate ( $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ ) that is formed by dissolution of MgO in the solution of  $\text{KH}_2\text{PO}_4$  and its eventual reaction to form the product according to the reaction



This product is the binder that can be used to form the matrix material to host wastes.

Wastes with a wide range of pH can be stabilized by this process and hence setting is possible with a range of feedstock from acidic to basic wastes. The process uses commercially available low-cost powders and mixing equipment and can be scaled up to any size and operations and carried out at waste sites with mobile equipment. The cost of treating wastes is low and comparable to that of cement grouting. No secondary waste streams are generated in the process and no volume increase occurs during stabilization. For these reasons, this technology is a good candidate for packaging OU4 waste streams at Fernald.

There have been earlier attempts to thermally treat the OU4 waste streams. Jantzen et al. [4], Janke et al., [5], and Merrill and Janke [6] have reported results on vitrifying simulated OU4 waste streams. The approach taken in our work is distinct from theirs. We demonstrate stabilization and packaging of actual Silo I waste at room temperature. The advantages of this approach are several:

- No secondary waste streams result from this process due to volatility of any components of the primary waste stream.
- Glovebox operation is easier because no heating elements are required.
- In general, the cost of this process is lower than that of vitrification [7].

The study was conducted in two steps. Surrogate waste formulated by FEMP experts was used in this study to tailor the process for maximum waste loading. The results were then used to fabricate waste forms with actual Silo I waste, which were evaluated using the standard Toxicity Characteristic Leaching Procedure (TCLP) [8]. While a large number of samples are being tested by FEMP for complete evaluation, we present here the results of the TCLP test performed in our

laboratory, because this test has been very conclusive in establishing that the CBPC process is one of the most suitable approaches for packaging Silo I waste.

### COMPOSITION OF SILO I WASTE

Considerable characterization work has been done on Silo waste streams. The general composition given by Jantzen et al. [4] is shown in Table 1.

Table 1. General composition of Silo I and II wastes

Nonhazardous components		Hazardous components	
Oxide	Wt. %	Oxide	Wt. %
Al <sub>2</sub> O <sub>3</sub>	3.7	BaO	6.3
CaO	1.5	PbO	12.3
Fe <sub>2</sub> O <sub>3</sub>	4.8	Oxides of	All at trace levels and in parts per million (ppm)
K <sub>2</sub> O	0.9	As <sup>5+</sup> ,	
MgO	1.7	Cr <sup>6+</sup> ,	
Na <sub>2</sub> O	1.7	Ni,	
P <sub>2</sub> O <sub>5</sub>	0.8	Se <sup>4+</sup> , and	
SiO <sub>2</sub>	62.9	Zn	

The data in Table 1 show that the main component in the waste is silica, which accounts for two-thirds of the waste stream. The Fe<sub>2</sub>O<sub>3</sub> (haematite) gives the waste its red color. In addition, alumina, lime, and alkali metals are present in low but significant concentrations.

The major hazardous components in the waste are lead and barium. Their very high concentrations make this waste very difficult to stabilize. Most of the lead is in the form of carbonate. In addition, the waste also contains other hazardous components such as nickel and zinc, and in addition, metals in higher oxidation states such as As<sup>5+</sup>, Cr<sup>6+</sup>, and Se<sup>4+</sup>. These metals in higher oxidation states are easily leachable, unless they are reduced during the stabilization process. One purpose of this work was to demonstrate stabilization of these metals in higher oxidation states.

## RADIOACTIVITY IN THE WASTE

The major radioactive component in the waste was radium ( $^{226}\text{Ra}$ ). Its specific activity was  $0.477\text{ }\mu\text{Ci/g}$ , and the total specific activity of all the isotopes in the waste was  $3.85\text{ }\mu\text{Ci/g}$ . This high activity was a concern while dealing with this waste in our laboratory. In particular, due to the high activity of radium, emanation of its gaseous daughter product radon ( $^{222}\text{Rn}$ ) into the laboratory atmosphere was a serious concern.

## SAMPLE PREPARATION

When the sealed container was received from FEMP, it was opened and exhaled in a fume hood for three days to allow the trapped radon to escape. The entire treatability study had to be performed in the fume hood. Each time, only a precalculated amount of waste was removed from the container and the remainder was kept in the closed container. The operators wore double layers of gloves. Before and after each session of the work, the room was surveyed to detect any stray contamination in the room; if detected, the room was decontaminated.

Our initial study was done with the surrogate waste provided by FEMP. It was a mixture of oxides that simulated the actual waste very closely. Determining treatability with the surrogate waste was necessary to avoid expensive failure with the real waste streams. Various waste loadings were attempted with the surrogate waste and, based on physical and mechanical properties, the highest waste loading was selected for the treatability study to be done with actual waste.

As shown in Table 2, the optimal waste loading achieved with the dry surrogate waste was 60.5 wt.%. At this level, the samples set well into homogeneous monoliths. The density of the samples was  $1.986\text{ g/cm}^3$ , and open porosity measured by the water intrusion technique was 4.8%. Compressive strength was 3318 psi; the land disposal requirements for compressive strength are only 500 psi and the strength obtained in our study is nearly one order of magnitude higher than that. Therefore, even this high waste loading was considered to be feasible and safe. Using this high loading as a guideline, we could make samples of the actual waste with a loading of 66.05 wt.%. This higher loading was possible partly because of the 19 wt.% water in the actual waste, which partly compensated for the stoichiometric water needed for the reaction represented in Eq. 1. As one may notice in Table 2, the total water content in the slurry of the actual waste was higher than that in the slurry of the surrogate waste. Despite this difference, the slurry of the actual waste had the same consistency as that of the slurry of the surrogate waste.

Table 2. Composition (wt.%) of test samples

Sample identity	Waste, dry	Waste, actual	Binder	Total water
Surrogate waste	60.5	NA <sup>a</sup>	26.2	13.3
Actual waste <sup>b</sup>	53.5	66.05	24	23.55

<sup>a</sup>NA: not applicable.

<sup>b</sup>Actual waste contains 19 wt.% of water.

A 5-gal concrete mixer placed in the fume hood was used for this study. The actual waste received from FEMP was first homogenized by mixing it for  $\approx 30$  min. The waste was then mixed with the binder powders and water, and the reactions were allowed to occur during mixing of the components for another 30 min. The resulting slurry was a smooth paste that could be poured into molds to form 2 x 2 x 2 in. cubes; or cylinders of 1.0 in. diameter. The slurry set in  $\approx 2$  h and formed hard samples. Slurry temperature rose to  $\approx 55$  °C during setting. The samples were allowed to cure for several weeks before they were removed from the molds and tested.

## EXPERIMENTAL RESULTS

The main criterion used for testing good packaging of a mixed waste is the Toxicity Characteristic Leaching Procedure (TCLP) [8]. To evaluate containment of the radioactive isotopes, we also tested the leachate for radioactivity at the end of the TCLP test. Normally, leaching of radionuclides is done by using American Nuclear Society's 16.1 90-day immersion test [9] on the monolithic sample. It is expected that FEMP will perform this test on a large number of samples made by us and provided to them. In our evaluation, however, because the leachate water was collected from crushed samples, the TCLP test was more severe and came closer to the worst-case scenario than did the ANS 16.1 immersion test. Results from the TCLP test are presented in Tables 3 and 4.

The TCLP results in Table 3 show that the samples passed the test at the UTS limits for all metals. This indicates that the phosphate bonded ceramic process is a very good candidate for stabilizing all of the hazardous metals shown in Table 3. In particular, the Pb concentration in the waste was  $\approx 12$  wt.% . As a result, at the dry waste loading of 53.5 wt.% in waste form, Pb content was 64,200 ppm in the waste form that was tested. In spite of this high content in the waste form, the Pb level in the leachate was below the detection limit of 0.1 ppm. This demonstrates the effectiveness of the process in stabilizing hazardous metals in the waste.

Table 3. TCLP results on stabilized samples (mg/L)

Contaminant	As	Cd	Cr	Co	Cu	Ni	Pb	Se	Sr
Level in leachate	0.22	<0.1	0.05	0.55	0.01	2.31	<0.1	0.82	0.13
UTS limit	5.0	0.2	0.85	-	-	13.6	0.75	5.7	-

Table 4 gives the specific activities in various samples, including those in the TCLP leachate. The total specific activity in the leachate was calculated on the basis of the measurement of alpha and beta activity in the leachate and then estimating the gamma activity as equal to that of beta. With this total specific activity of the leachate, we could then estimate the total activity in the leachate, which was 20 times (by weight) that of the waste form subjected to the leaching procedure. This amounted to 4.42  $\mu\text{Ci/g}$  of the waste form. When this is compared with the specific activity in the waste (2.06  $\mu\text{Ci/g}$ ), one finds that the leaching activity is lower by three orders of magnitude, or containment of the radioactive isotopes due to stabilization of the waste by the phosphate bonded ceramic process is higher by three orders. The radium content in the waste was 0.477  $\mu\text{Ci/g}$ . Because radium is water-soluble, the leachate would be a pathway for it. Despite this, the leachate activity is extremely low, implying that the radium and most other isotopes are well stabilized in the waste forms. This is possible because radium would form its insoluble phosphate form in the leachate; hence, the chemically bonded phosphate process is a good method for arresting leaching of radioactive contaminants.

Table 4. Specific activities ( $\mu\text{Ci/g}$ ) in various samples<sup>a</sup>

Sample code	Alpha	Beta	Total
Waste as received			
Total specific activity	---	---	3.85
Specific activity of $^{226}\text{Ra}$	---	---	0.477
Calculated activities in waste form			
Total specific activity	---	---	2.06
Specific activity of $^{226}\text{Ra}$	---	---	0.255
Specific activities in TCLP leachate (pCi/g)	$25 \pm 2$	$98 \pm 10$	$221 \pm 22^a$

<sup>a</sup>As an approximation, we have assumed that activity of gamma radiation is nearly equal to that of beta activity.

## DISCUSSION AND CONCLUSIONS

This study has demonstrated that the CBPC process has the potential for stabilizing both hazardous contaminants and radioactive isotopes from the Fernald Silo I waste. High waste loadings of  $\approx 60$  dry wt.% and  $\approx 66$  actual wt.% are feasible. Even at such high waste loadings, contaminant concentrations in the TCLP leachates have remained well below the UTS limit. This implies that the above waste loadings may be used for packaging the Silo wastes.

Even at the higher waste loading of 66 wt.%, there is no effective increase in volume of the waste form. The waste forms had the same volume as that of the waste. The binders simply occupied the space of the voids in the waste. This means that disposal costs are not increased because of the stabilization.

The Silo wastes, though low-level waste streams, are difficult to handle because of the radon emanation. Several difficulties were encountered while handling this waste. For example, radon accumulated in the closed containers. Therefore, while opening the container, care had to be taken to ensure that radon did not diffuse into the room.

During storage and handling of the samples, we also noted that radon permeated through the airtight polyethylene bags. This indicates that such bags are probably not suitable for handling this waste or its waste forms. And because the contamination might have permeated through a single glove layer, double gloves and double shoe covers were used by the workers.

Aside from these problems related to the activity of the waste, the surrogate waste and the actual waste behaved very similarly during stabilization. For future work on this waste with the CBPC process, the surrogate formulation used in this study is very appropriate.

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